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Registry No. 1, 81277-27-2; $(\mu\text{-H})_2Rh_2\{P[N(CH_3)_2]_3\}$, 81277-05-6; $\{ClRh(C_2H_4)_2\}_2$, 12081-16-2; tris(dimethylamino)phosphine, 1608-26-0.

Supplementary Material Available: Preparation of the $(HRhP_2)_2$ dimer and characterization of **1**, three tables listing atomic coordinates, selected bond distances and angles, and thermal parameters for nonhydrogen atoms in crystalline $H_4Rh_2\{P[N(CH_3)_2]_3\}_4$, and Figure 2, a full-perspective ORTEP drawing of the tetrahydride **1** (11 pages). Ordering information is given on any current masthead page.

Temperature-Regulated Release of Alkali Metal Salts from Novel Polymeric Crown Ether Complexes[1]

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Early studies[3] on the thermodynamics of cation–macrocyclic crown ether interaction have shown that $\Delta H°$ and $\Delta S°$ values for complexation are usually negative and small.[4] Consequently the sign and value of the free energy, $\Delta G°$, may depend on the absolute temperatures, since $\Delta G° = \Delta H° - T\Delta S°$. In homogeneous systems this has little significance. However, in a heterogeneous system, such as equilibria between insoluble polymer and solution, it is reasonable to assume that the opposing effects of $\Delta H°$ and $\Delta S°$ could be exploited to induce temperature-regulated release of salts from their insoluble polymeric crown ether complexes, as follows:

$$[P]\text{-}(CE) + MX \underset{T_2}{\overset{T_1}{\rightleftharpoons}} [P]\text{-}(CE)MX \qquad T_2 > T_1$$

[P] = polymer, CE = crown ether, M = alkali metal, X = halide

Polymeric materials carrying pendant crown ether groups have been prepared by: (i) direct polymerization of vinylbenzo crown ethers;[5] (ii) condensation polymerization of dibenzo crown ethers with formaldehyde.[6]

Recently, we presented a different approach, based on a one-step in situ cyclization reaction.[7] Thus, a nucleophilic substitution reaction between two electrophilic centers (benzyl halide groups, part of the polymeric matrix) and a cation-templated polyglycol takes place, leading to large macrocycles. The so-called "pseudo crown ether" anchored to a macroporous matrix structure showed high affinity for transition-metal complex anions (in their conjugate acid form), with excellent reversibility in complexation–decomplexation.

Now this approach has been extended to the synthesis of polymeric crown ethers carrying pendant macrocyclic rings. This was accomplished by reversing the role of the functional groups and putting the nucleophilic centers on the polymeric matrix.

Scheme I

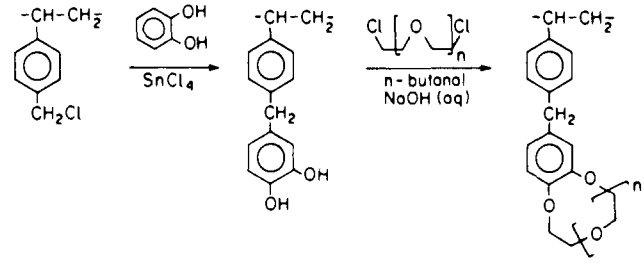

Table I. Synthesis of Polymeric Crown Ethers by Condensation of Polymer-Bound Catechol and Polyglycol Dihalides

			molecular fraction of unit		
polymer	no.	glycol dihalide	$-C_6H_4CH_2Cl$	$-C_6H_3(OH)_2$	$-C_6H_3$ crown
crown-4	NK-37	triethylene	0.08	0.22	0.65
crown-5	NK-40	tetraethylene	0.04	0.21	0.64
crown-6	NK-41	pentaethylene	0.02	0.21	0.60
crown-8	NK-43	heptaethylene	0.00	0.27	0.86

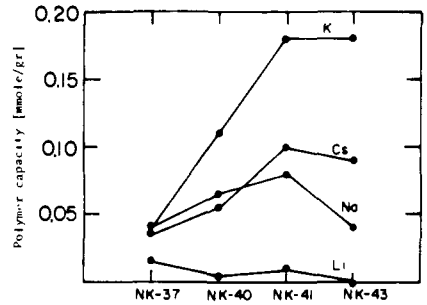

Figure 1. Ion recognition patterns for polymeric crown ethers (see Table I) expressed as polymer capacity from 0.01 M solutions in CH_3OH at 20 °C.

Thus, the alkylation of catechol with (chloromethyl)styrene–divinylbenzene copolymer (see Scheme I), produces the polymer-bound catechol, which upon reaction with a series of polyglycol dihalides affords macrocyclic polymeric benzo crown ethers in fair yields.

The degree of conversion of the catechol groups into macrocyclic ether groups and the residual concentration of diol groups were estimated from elemental analysis, weight-gain data, and the analysis of dinitrophenyl derivatives of the residual diol groups. The description and properties of the polymeric crown ethers are presented in Table I.

Next, the ion-coordination patterns for the polymeric crowns were determined by using distribution and column techniques. Equilibrium distribution values in methanol in the temperature range 20–60 °C, for the perchlorate, thiocyanate, or bromide salts, have led to the following conclusions: (1) The spheric recognition patterns, typical of crown ethers in solution, are fully reproduced in the polymeric analogues. Figure 1 shows the relative ion capacities for polymeric benzo crown-4, crown-5, crown-6, and crown-8. Accordingly, the order of binding constants is K > Cs > Na > Li for polymeric benzo crown-6 and benzo crown-8 and K > Cs ≃ Na > Li for polymeric benzo crown-4 and benzo crown-5. (2) The highest binding constants are for polymeric benzo crown-6, as anticipated from data for the corresponding benzo crown-6.[3] (3) The polymers bind alkali metal cations by two mechanisms: the residual catechol groups by an ion-exchange mechanism, and the crown groups by a salt-coordination mechanism; the second mechanism is temperature dependent. Consequently, a column packed with polymeric benzo crown-6 can be saturated with KCl, and as Figure 2 shows, a sudden thermal increase of 40 °C causes a spontaneous elution, by "thermal shock", and a 3-fold increase in the eluant of the original ion concentration. Quantitative release of all the bound salt is observed.

(1) Presented at the Second Chemical Congress of the North American Conference, San Francisco, CA, August 24–29, 1980.
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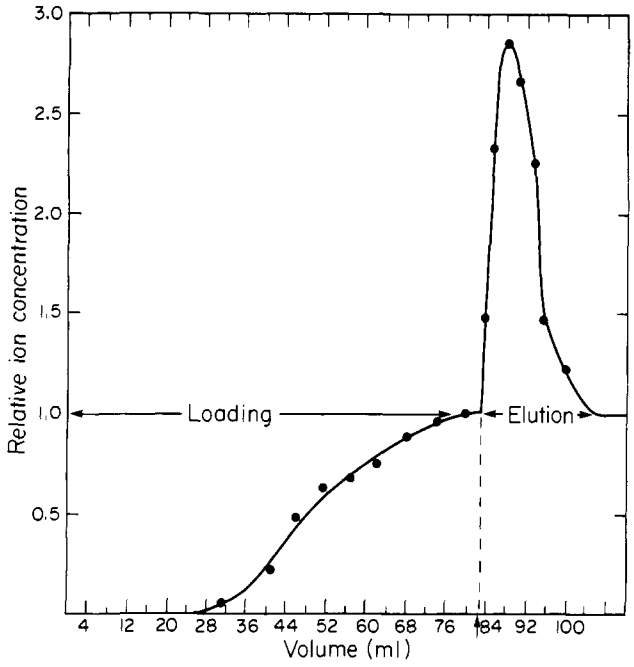

Figure 2. Spontaneous ion elution from polymeric crown ether-6 (N-K-41) by thermal shock at 60 °C in CH_3OH.

In conclusion, a polymeric crown ether system was found in which ion complexation is completely reversible and temperature dependent. This phenomenon should be of considerable interest in (i) water desalination processes by polymeric crown ethers as membranes, (ii) temperature effects in nucleophilic displacement reactions in phase-transfer catalysis by polymer-bound activated anions (e.g., [P]–CE·NaCN), and (iii) thermoregulated polymeric delivery systems for Na/K.

Registry No. (Chloromethyl)styrene divinylbenzene copolymer, 9036-15-1; catechol, 120-80-9; triethyleneglycol dichloride, 112-26-5; tetraethyleneglycol dichloride, 638-56-2; pentaethylene glycol dichloride, 5197-65-9; heptaethyleneglycol dichloride, 56930-39-3; K^+, 24203-36-9; Cs^+, 18459-37-5; Na^+, 17341-25-2; Li^+, 17341-24-1.

Intrastrand Cross-Linking of the Guanines of the Deoxytrinucleotide d(G-C-G) via *cis*-$Pt(NH_3)_2Cl_2$

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Binding of the antitumor drug *cis*-$Pt(NH_3)_2Cl_2$ (*cis*-Pt) to DNA is supposed to be a main event in its mechanism of action.[1] The kinetically most favored binding sites are the N7 atoms of the guanine bases.[2] Much evidence is accumulating that a bifunctional binding of *cis*-Pt between bases of the same strand is the predominant lesion. Generally, binding between adjacent guanine bases is considered most likely,[3] and there is evidence that such a binding in di- and tetranucleotides is possible.[4,5] However, alternative binding possibilities have been suggested, including intrastrand binding to two guanines separated by one or more other bases.[6,7] Particularly, a recent genetic study to determine the base-pair substitutions caused by *cis*-Pt in the *lacI* gene of *E. Coli* mutants showed that the majority of the substituted bases were originally part of a GAG or GCG nucleotide sequence.[7] To determine whether a cross-link between the two guanines of such a sequence is possible we have studied the interaction between *cis*-Pt and the deoxytrinucleotide d(G-C-G).

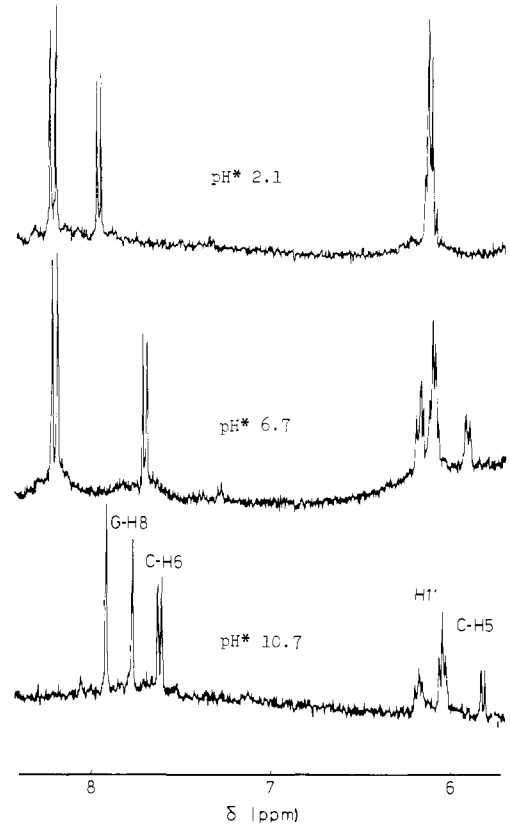

Figure 1. Part of the 360-MHz ^1H NMR spectra (8.5–5.5 ppm) of d(G-C-G)·*cis*-Pt at various pH* (pH* denotes uncorrected meter readings of solutions in D_2O). Due to the applied method for reduction of the residual HDO resonance,[13] the relative intensities of the resonances around 6 ppm are slightly smaller than those of the resonances around 8 ppm.

cis-Pt was allowed to react with 1 equiv of d(G-C-G) (Na^+ form) at room temperature for 2 weeks (concentration 10^{-5} M; pH between 6 and 7). The main product from Sephadex G-25 and Sephadex G-10 gel chromatography (accounting for approximately 90% of the total optical density at 260 nm) was isolated. Comparison of the Sephadex G-25 chromatograms of free d(G-C-G) and of its platinum adduct shows that the latter is monomeric. Platinum analysis agreed with the presence of one platinum per trinucleotide.[8] ^1H NMR spectra show that the isolated product (d(G-C-G)·*cis*-Pt) is almost pure (Figure 1). Because both cytosine N3 and guanine N7 are reported to be binding sites for platinum,[4,9] the actual binding sites were de-

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(8) A solution containing d(G-C-G)·*cis*-Pt was analyzed for Pt by flameless atomic absorption spectroscopy. From comparison with the UV absorption at λ_{max} (260 nm), an ϵ_{max} of about 24 000/mol of platinum is calculated. This value agrees with the presence of one *cis*-Pt per trinucleotide, taking into account a decrease of ϵ_{max} of about 10–20% upon binding of *cis*-Pt.[4,10]
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